CHEM 371: Lecture 3

Having seen how to extremize functionals in Lecture 2, we're now in a position to apply the procedure to the expression for the action *S*, which you'll recall is given by

$$S = \int_{t_1}^{t_2} dt L(\mathbf{q}_1, \ldots, \mathbf{q}_N, \dot{\mathbf{q}}_1, \ldots, \dot{\mathbf{q}}_N) \tag{1}$$

The extremization of *S* leads to these conditions on the positions and velocities:

$$\frac{\partial L}{\partial q_{i\alpha}} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_{i\alpha}} = 0, \qquad i = 1, 2, \ldots, N, \qquad \alpha = 1, 2, 3 \tag{2}$$

which are the so-called Euler-Lagrange equations. In 3-d they lead to $3N$ second order differential equations, and if these equations are supplemented by $6N$ initial conditions on the positions and velocities, they can in principle be solved. (When the coordinates are Cartesian, the α refer to *x*, *y* and *z* components.)

As an illustration of the application of the above Lagrangian formalism to a specific system, consider the dynamics of a single mass point in 3-d in the presence of a conservative potential (i.e., a potential that depends only on positions, not velocities.) When Cartesian variables are used to describe the system, the kinetic and potential energies are given by

$$K = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \tag{3a}$$

and

$$V = V(x, y, z) \tag{3b}$$

After constructing the Lagrangian of this system as $L = K - V$, and then extremizing the associated action following the methods just described, the resulting E-L equations are

$$m\ddot{x} = -\frac{\partial V}{\partial x} = F_x, \quad m\ddot{y} = -\frac{\partial V}{\partial y} = F_y, \quad \text{and} \quad m\ddot{z} = -\frac{\partial V}{\partial z} = F_z$$

which are nothing but Newton's laws. The important point to note here is that the form of the dynamical equations – as given in Eq. (2) – are not changed by the use of non-Cartesian coordinates.

● Hamiltonian Dynamics

Although Lagrangian dynamics removes the special status that Newtonian mechanics attaches to Cartesian coordinates, it can still be difficult to apply because the second order differential equations that describe its equations of motion aren't always easy to solve. So Hamilton developed another formulation of classical mechanics based on first order differential equations. His approach also takes the Lagrangian *L* as its starting point, but replaces the independent variables $\dot{q}_{i\alpha}$ in that expression by new independent variables $p_{i\alpha}$ called generalized or conjugate momenta, defined as the slope of *L* with respect to $\dot{q}_{i\alpha}$. That is,

$$p_{i\alpha} = \frac{\partial L}{\partial \dot{q}_{i\alpha}}, \qquad i = 1, 2, \ldots, N, \qquad \alpha = 1, 2, \ldots \tag{4}$$

The new function *H* that has $p_{i\alpha}$ and $q_{i\alpha}$ as the independent variables instead of $\dot{q}_{i\alpha}$ and $q_{i\alpha}$ is defined as follows

$$H = \sum_{i=1}^{N} \sum_{\alpha} \dot{q}_{i\alpha} p_{i\alpha} - L, \tag{5}$$

and it becomes a function solely of the $p_{i\alpha}$ and $q_{i\alpha}$ once the $\dot{q}_{i\alpha}$ are eliminated from (5) using the definitions in (4). The function *H*, referred to as the *Hamiltonian* of the system, is said to be the Legendre transform of *L* with respect to the $3N$ $\dot{q}_{i\alpha}$,

We've encountered Legendre transforms before, most notably in thermodynamics, where they are used to define new thermodynamic potentials that contain the same information as the so-called fundamental equation, this equation being a relation between the energy *U* of a system and its entropy *S*, volume *V* and number of particles *N*, i.e.,

$$U = U(S, V, N) \tag{6}$$

This is a fundamental equation in the sense that knowing this equation, one knows everything one can know about the thermodynamics of the system. But because the independent variables in this equation aren't always the most easy to control in experimental settings (*S* in particular), it helps to have equivalent representations of this equation in which the independent variables are more experimentally accessible, like temperature or pressure. Now *T* is just the slope of *U* with respect to *S*, i.e., $T = (\partial U / \partial S)_{V,N}$, and we can construct a new function, say, *F*, that has *T* as an independent variable in place of *S* by means of the Legendre transform. The definition of this new function is

$$F = U - TS \tag{7}$$

and you will, of course, recognize it as the definition of the Helmholtz potential. F becomes a function of T, V and N once S is eliminated from (7) using U from (6) and the definition of the slope. Once that's done we have $F = F(T,V,N)$, which is also a fundamental relation, and all the thermodynamic properties of a system can be derived from this relation too. (For more on Legendre transforms in the context of thermodynamics, read Sec. 5-2 in Callen.)

More than one variable in the fundamental equation of (6) can be eliminated in favour of the corresponding slopes; for instance, both S and V can be eliminated from (6) in favour of T and P, where P, the pressure, is given by

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{8}$$

To construct a function (say, G) with T and P (and N) as the independent variables and that is equivalent in content to Eq. (6), we Legendre transform U with respect to S and V according to the definition

$$G = U - TS - (-P)V = U - TS + PV \tag{9}$$

which identifies G as the Gibbs potential. G becomes a function of T, P and N, i.e., $G = G(T,P,N)$, once S and V are eliminated from (6) and (9) using the definitions of T and P. This expression for G is also a fundamental relation, and it also tells you everything you can know thermodynamically about the system.

● In the same way, the Hamiltonian of Eq. (5) is equivalent to the Lagrangian but is expressed in terms of new independent variables:

$$H = H(\{p_{i\alpha}\},\{q_{i\alpha}\},t)$$

What are the equations of motion that we derive from this function? They can be derived, as before, from the principle of least action, which – from our earlier discussions – amounts to the requirement that

$$\int_{t_1}^{t_2} dt\delta L = 0 \tag{10}$$

where δL is the variation in L. From Eq. (5), this variation (assuming for simplicity that L has no explicit time dependence) is given by

$$\delta L = \delta\left(\sum_{i,\alpha} p_{i\alpha}\dot{q}_{i\alpha}\right) - \delta H$$

$$= \sum_{i,\alpha} (\delta p_{i\alpha} \dot{q}_{i\alpha} + p_{i\alpha} \delta \dot{q}_{i\alpha}) - \sum_{i,\alpha} \left(\frac{\partial H}{\partial q_{i\alpha}} \delta q_{i\alpha} + \frac{\partial H}{\partial p_{i\alpha}} \delta p_{i\alpha} \right)$$

$$= \sum_{i,\alpha} \left(\delta p_{i\alpha} \dot{q}_{i\alpha} + p_{i\alpha} \frac{d}{dt} \delta q_{i\alpha} - \frac{\partial H}{\partial q_{i\alpha}} \delta q_{i\alpha} - \frac{\partial H}{\partial p_{i\alpha}} \delta p_{i\alpha} \right) \tag{11}$$

Eq. (11) is now substituted into Eq. (10), and the term involving $d\delta q_{i\alpha}/dt$ is integrated by parts. The surface term obtained from this partial integration is $p_{i\alpha} \delta q_{i\alpha}|_{t_1}^{t_2}$, which vanishes by virtue of the fact that $\delta q_{i\alpha}(t_2) = \delta q_{i\alpha}(t_2) = 0$. So Eq. (10) reduces to

$$\sum_{i,\alpha} \int_{t_1}^{t_2} dt \left[\delta p_{i\alpha} \left(\dot{q}_{i\alpha} - \frac{\partial H}{\partial p_{i\alpha}} \right) - \delta q_{i\alpha} \left(\dot{p}_{i\alpha} + \frac{\partial H}{\partial q_{i\alpha}} \right) \right] = 0 \tag{12}$$

which can only be satisfied for arbitrary variations of $p_{i\alpha}$ and $q_{i\alpha}$ if

$$\dot{q}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}}, i = 1, \ldots, N, \quad \alpha = 1,2, \ldots. \tag{13a}$$

and

$$\dot{p}_{i\alpha} = -\frac{\partial H}{\partial q_{i\alpha}}, i = 1, \ldots, N, \quad \alpha = 1,2, \ldots. \tag{13b}$$

These are Hamilton's equations of motion, and they correspond to 6*N* first order differential equations. So if one is given 6*N* initial conditions on the positions and momenta, these equations can be solved, in principle, for any future time *t*. These first order equations are often easier to solve than Lagrange's second order equations.

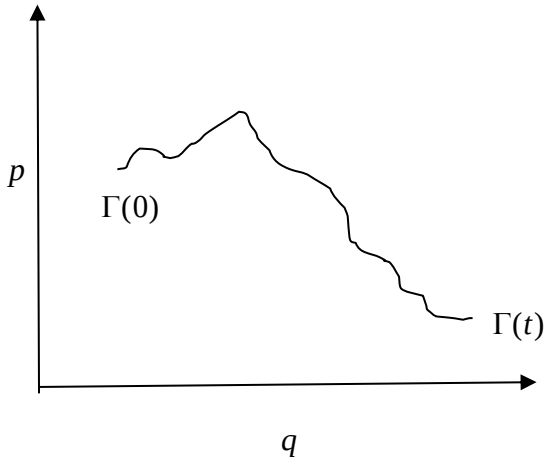
It is the Hamiltonian form of the equations of motion that we will appeal to in our study of time-dependent statistical mechanics because they are expressed in terms of the variables – positions and momenta – that are used to specify the microstates of a system.

● Phase Space Dynamics

Recall that to calculate a time correlation function we said we needed expressions for the probability $P(\Gamma)$ and the function $A(t;\Gamma)$. We now know how the positions and momenta of individual particles in a system evolve in time, and now we'd like to know how the system as a whole, consisting of *N* particles, evolves in time. That is, we're interested in the fate of the microstate $\Gamma = \{\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N\}$ as time progresses.

In the $6N$ dimensional space that defines phase space, the microstate Γ is a single point at a given instant of time. At some later time, the positions and momenta assume new values, and so Γ moves to a new point in phase space. As time continues to advance, the successive points in phase space that correspond to the new locations of Γ trace out a trajectory called the phase space trajectory. This trajectory is uniquely determined by the microstate at the starting time because the equations of motion of the $\mathbf{p}_i$'s and $\mathbf{q}_i$'s are deterministic. In other words, two points in phase space with distinct initial conditions produce distinct non-intersecting trajectories. The trajectories don't intersect because if they did it would mean that from the point of intersection onwards, the trajectories would end up in different final states, which contradicts the uniqueness of the solutions to the equations of motion.

The figure below is a schematic drawing of a phase space trajectory that evolves from some microstate at $t = 0$ to one at $t = t$.



● Example of a phase space trajectory

There is one system for which the phase space trajectory can be determined exactly: this is a single harmonic oscillator in $1d$, and it's instructive to work through the details of its dynamics. A harmonic oscillator is any object that moves back and forth about an equilibrium position with a constant amplitude and a constant frequency (which is independent of the amplitude.) When displaced from its equilibrium position, a harmonic oscillator experiences a restoring force F that is linear in the displacement. That is,

$$F = -kx$$

where k is a constant that is a measure of how strong the tendency is for the oscillator to be restored to its original position. If we were to use Newton's laws to describe the dynamics of the oscillator, we would work with the following equation:

$$m\ddot{x} = -kx$$

which is easy to solve, but we'll consider these dynamics from the point of view of Hamiltonian mechanics. For this purpose, we'll need the system's Lagrangian, which in turn requires expressions for the kinetic and potential energies of the oscillator. The kinetic energy K is given by the familiar relation

$$K = \frac{1}{2} m\dot{x}^2$$

The potential energy V is related to F by the equation $F = -\partial V / \partial x$, and so by integration we obtain (after setting the arbitrary integration constant to 0)

$$V = \frac{1}{2} kx^2$$

The Lagrangian is therefore

$$L = K - V = \frac{1}{2} m\dot{x}^2 - \frac{k}{2} x^2$$

The corresponding Hamiltonian H is obtained using a Legendre transform to eliminate $\dot{x}$ in L in favour of its conjugate variable $p \equiv \partial L / \partial \dot{x} = m\dot{x}$. From the definition of Legendre transforms we have

$$\begin{aligned} H &= \dot{x}p - L \\ &= \dot{x}p - \frac{1}{2} m\dot{x}^2 + \frac{k}{2} x^2 \\ &= \frac{p}{m} p - \frac{m}{2}\left(\frac{p}{m}\right)^2 + \frac{k}{2} x^2 \\ &= \frac{1}{2m} p^2 + \frac{k}{2} x^2 \end{aligned}$$

We can now determine the equations of motion; they are

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}$$

and

$$\dot{p} = -\frac{\partial H}{\partial x} = -kx$$

These are two first order ordinary differential equations, and once we specify their initial conditions (which correspond to assigning definite values to x and p at $t = 0$), they're readily solved for x and p as a function of t. But we're more interested in the system's phase space trajectory (the variation of p with x), and it turns out that to calculate this function we don't really need to explicitly solve the equations of motion. What we do instead is the following: first rewrite the equations of motion as

$$m dx = p dt$$

and

$$dp = -kx dt$$

Then divide one equation by the other, to get

$$m \frac{dx}{dp} = -\frac{p}{kx}$$

This equation can be solved by first separating the variables as

$$mkx dx = -p dp$$

and then integrating, which leads to

$$mk \frac{x^2}{2} = -\frac{p^2}{2} + C$$

where C is a constant of integration. This equation can be rearranged to

$$\frac{1}{2m} p^2 + \frac{k}{2} x^2 = \frac{C}{m} \equiv C'$$

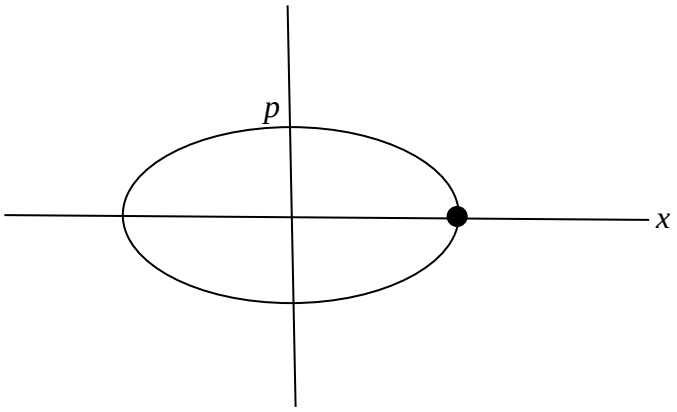
From the structure of the LHS of this equation, it's obvious that the integration constant C' is nothing but the total energy of the system U. That is,

$$\frac{1}{2m} p^2 + \frac{k}{2} x^2 = U$$

This is the required equation for the phase space trajectory, and it corresponds to the equation of an ellipse, which is defined as

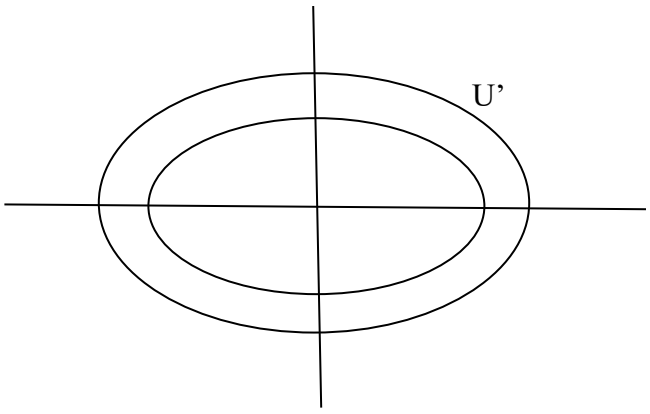
$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$

So the phase space trajectory will look like this



But this trajectory also has a direction associated with it, meaning the phase points move in either a clockwise or anti-clockwise direction as time increases at fixed U. Which of these two directions is selected can be worked out. Imagine displacing the oscillator from its equilibrium position to its maximum extension in the positive (rightwards) x direction. When it reaches this point, its velocity is 0, and the phase point corresponding to this situation is shown as the black dot on the figure above. If the oscillator is now released, it starts moving to the left, that is, in the negative x direction, so its velocity decreases. This particular direction corresponds to a clockwise movement of the phase point along its elliptical trajectory.

A few points to note: The constant energy U of this oscillator represents its macrostate, while every point on the ellipse represents one of its possible microstates having this energy. The phase space trajectory of an oscillator with a different energy, say $U' > U$, would follow a different elliptical trajectory, but it would be concentric with the first (since phase space trajectories cannot intersect.) Specifically,



The shape of these trajectories makes it clear that no matter where the system starts out from initially, eventually it returns to its starting point, which is what you would expect of an object that executes periodic motion. The time it takes to do this can be calculated from the actual solutions to the equations of motion (which are trigonometric functions.)